

Activated alumina in fluorine ion adsorption regeneration in the experimental study of brackish water in Fuxin

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Keywords: The adsorption; regeneration; coagulant; Activated alumina

Abstract. Through static tests, this thesis studies the ability of activated alumina for absorbing the fluoride ion in fluorine-containing bitter salty water at Fuxin area, and fluoride ion in the regenerated liquid formed in a way that the original water sample is treated in a regeneration way with aluminum sulfate solution is removed with a coagulating precipitation method. Through comparison, this thesis analyzes the influence of different filter materials and coagulant varieties on the fluoride ion removal effect in fluorine-containing effluent, and also studies the influence of the concentration of regenerant aluminum sulfate solution and regeneration time on the regenerating effect of activated alumina. The study shows that as the filter material, the activated alumina has a good effect on removing the fluoride ion in the water sample, and the removal rate is 66.51%. On the same condition, as the coagulant, calcium chloride of the same mole quantity has the best effect on removing the fluoride ion, and the fluoride ion removal rate is 82.93%. On the conditions that the water temperature is 15°C, the concentration of aluminum sulfate is 3%, the regeneration time is 3h and the regeneration velocity is 3m/k, the regeneration effect is the best, and the regeneration rate reaches 95.10%.

Introduction

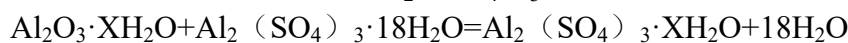
Fluorine is one of the necessary microelements of human bodies. It is the best for an adult to take in fluorine of 2-3 mg normally every day, and too much or too less fluorine take-in quantity would cause diseases. In the drinking water, if the mass concentration of fluorine is less than 0.5mg/L, saporidontia would be caused; if the mass concentration is more than 1.5mg/L, metabolic disturbance of calcium and phosphorus would be easily caused, which would lead to fluorosis, dental fluorosis or skeletal fluorosis and so on^[1]. In the drinking water, it is best that the mass concentration of fluorine is between 0.5 and 1.0 mg/L. In our country, high fluorine-containing effluent is distributed very extensively, and diseases caused by high fluorine-containing quantity are distributed at 27 provinces, cities and municipalities, especially remote areas such as northwest and northeast and rural areas where the economic development speed is relatively low^[2]. There are a lot of studies of fluoride ion removal in drinking water at home and abroad^{[3]-[4]}. Wherein, activated alumina is recommended, in the US, as the best available technology for removing a plurality of inorganic ions including fluoride^[5]. Activated alumina adsorbent is durable and nontoxic, and has high strength, a long life time, stable property and higher absorption capacity. The water quality meets the sanitary standards prescribed by the nation after activated alumina adsorbent is used for removing fluorine^[6]. Some studies show that regenerated liquid soaked by aluminum sulfate solution can evidently improve the absorption performance of activated alumina. In the studies at home and abroad, this method is a more mature effective way applied to the treatment of fluorine-containing water now^[7].

On this basis, this thesis studies the ability of activated alumina for absorbing the fluoride ion in fluorine-containing bitter salty water at Fuxin area, and fluoride ion in the regenerated liquid formed in a way that the original water sample is treated in a regeneration way with aluminum sulfate solution is removed with a coagulating precipitation method, which establishes a stable basis for the practicability of fluoride ion removal technique.

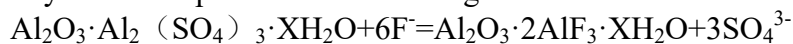
The principle for removing fluoride ion by means of activated alumina

The principle for removing fluoride ion by means of activated alumina is taken as the dual functions of ion exchange and physical absorption

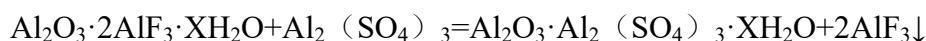
Activated transformation of $\text{Al}_2(\text{SO}_4)_3$ solution



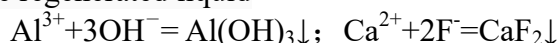
Physical absorption and ion exchange of adsorbent



The activation principle of adopting aluminum sulfate solution for regenerating activated alumina adsorbent



The principle of adopting calcium salt for chemical coagulation precipitation of fluoride ion in the regenerated liquid



Test material

Activated alumina used in this test is white globular porous particle. The particle size is even. The surface is smooth. The mechanical strength is high. The hygroscopicity is strong. The activated alumina has a lot of capillary channels and the superficial area is big. It has stronger absorption performance for fluoride ion. See the relative indexes in Table 1.

Tab.1 Activated alumina parameters

Indicators project	unit	Activated alumina
Particle size	mm	1-3
Bulk density	g/cm^3	0.60-0.80
Intensity	N 粒	≥ 35
Specific surface area	m^2/g	≥ 280
entrance	cm^3/g	≥ 0.35
Amount of fluoride	$\text{mg}/\text{gAl}_2\text{O}_3$	2.1

According to the provided effluent sample, see the water quality indexes of the measured original water sample in Table 2.

Tab.2 Raw water water quality index

Indicators project	COD (mg/L)	SS (mg/L)	pH	F— (mg/L)
Raw water	138.97	182	8.02	21.5

Test method

Activated alumina (particle diameter 0.2-0.4 mm), aluminum sulfate, calcium chloride. Fluoride ion selective electrode

Containing fluorine water samples taken from fuxin containing fluorine bitter salty water. Determination of the content of fluorine ion in water by fluorine ion selective electrode method.

Experiment method

In plug taper bottle, to join the activated alumina, add 1 l fluoride wastewater, the temperature is 20°C and the pH is 7 conditions, every 1 d oscillation 20 min, 3 d after the determination of residual fluorine ion concentration in the solution.

According to the amount of adsorption is calculated under type:

$$Q = (c_0 - c) \cdot v$$

Type of q - adsorption quantity, mg/g ;

c_0 , c - before and after the adsorption of fluoride ion concentration, mg/L;
 V - raw water volume, mL;

Test results

On the conditions that the water temperature is 15°C and PH is 7, activated alumina of 10g with particle size between 1 and 3 mm, zeolite of 10g, and sample filter material of 10g are respectively thrown in 3 beakers of 1000 ml with original water of 1L contained. The 3 kinds of mixtures are let stand for 2 days. Fluoride ion concentration in the supernatant is measured, and the corresponding absorption quantity is calculated so as to determine the best filter material for removing fluoride ion.

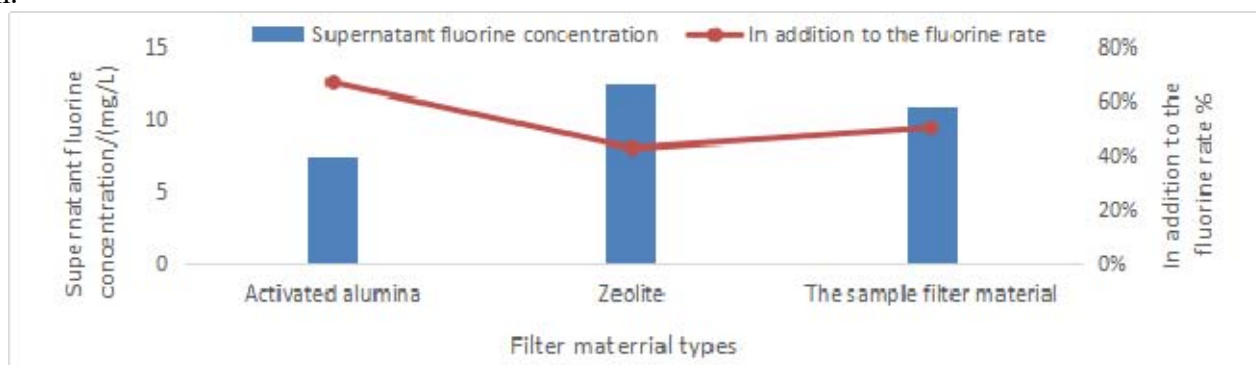


Fig. 1 Three kinds of filter material of removing fluorine ions in raw water

Figure 1 shows that on the same test conditions, the fluoride ion removal quantity of the three kinds of filter materials of the same particle sizes are the following: activated alumina: 1.43mgF/g, zeolite: 0.91mgF/g, and sample filter material: 1.07mgF/g. On the condition that the fluoride ion concentration in the original water is 21.5mg, the corresponding fluoride ion concentration in the supernatant are respectively 7.2mg/L, 12.4mg/L and 10.8mg/L, and the fluoride ion removal rate are respectively 66.51%, 42.33% and 49.77%.

On the condition of room temperature of 16°C, four portions of aluminum sulfate solution which has the same quantity and has concentration of 1%, 2%, 3% and 4% are respectively added in 4 beakers of 1000ml containing absorbing saturated activated alumina. The four kinds of aluminum sulfate solution are soaked for 3h, and the absorbing saturated activated alumina are regenerated. The regenerated activated alumina treated by the aluminum sulfate solution of 4 kinds of concentration is tested for absorption, and the absorbing quantity of the regenerated activated alumina is measured so as to determine the best concentration of the aluminum sulfate.

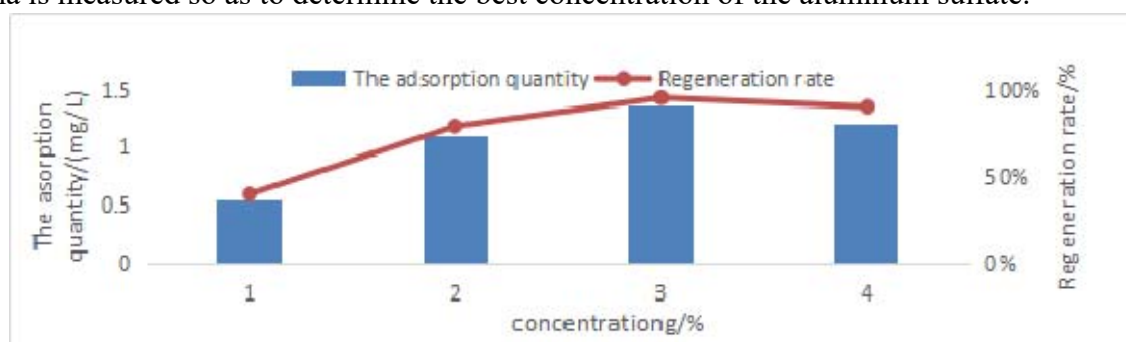


Fig.2 Aluminium sulfate solution concentration on the absorption effect of the activated alumina regeneration

Figure 2 shows that on the same test conditions, the regenerated absorbing quantity of the activated alumina treated by aluminum sulfate solution of 3% concentration has the most recovery. The absorbing quantity recovers to 1.36mg/g and the regeneration rate is 95.10%. When the concentration of the aluminum sulfate solution is too much, under the action of strong acid, the strength of aluminum oxide is lowered and collosol state occurs, and thus the regeneration effect is influenced. If the concentration of the aluminum sulfate solution is too low, the regeneration effect

is not evident. Thus, when used as regenerant, the concentration of aluminum sulfate should be controlled within a certain scope. Aluminum sulfate with the concentration of 3% is the best.

On the conditions that water temperature is 15°C and the concentration of aluminum sulfate is 3%, the three kinds of regeneration time are respectively 1h, 2h, 3h and 4h, and the absorbing saturated activated alumina are regenerated. Three portions of regenerated activated alumina of 10g are respectively taken out at different time for regenerating absorption tests. The absorption content of the regenerated activated alumina is measured so as to determine the best regeneration time.

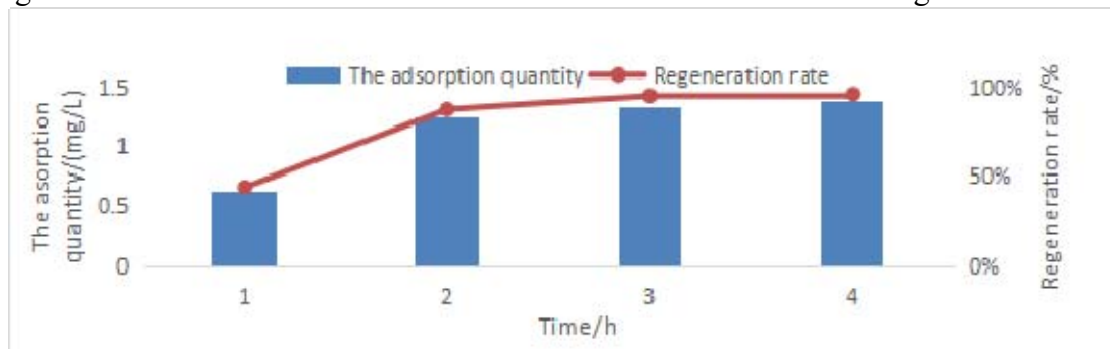


Fig.3 Time of activated alumina regenerative adsorption effect

Figure 3 shows that on the same test conditions, when the regeneration time is 3h, the absorption quantity recovers to 1.36mg/g and the regeneration rate is 95.10%. If the regeneration time is prolonged continuously, the enhancement degree of the regeneration absorption quantity of the activated alumina and the regeneration rate does not changed much. The comparison of regeneration time of 1h and 2h shows that the corresponding regeneration absorption quantity is respectively 0.63mg/g and 1.25mg/g, and the regeneration rate is respectively 44.06% and 87.41%. Thus 3h is determined as the best regeneration time of activated alumina.

On the conditions that water temperature is 15°C, the filtering column of the regenerating activated alumina is of 1.2m height, the concentration of aluminum sulfate is 3% and the regeneration time is 3h, the five kinds of regeneration velocity are respectively controlled to 2m/h, 3m/h 4m/h and 5m/h, and the absorbing saturated activated alumina are regenerated. The absorbing content of the regenerated activated alumina is measured so as to determine the best velocity.

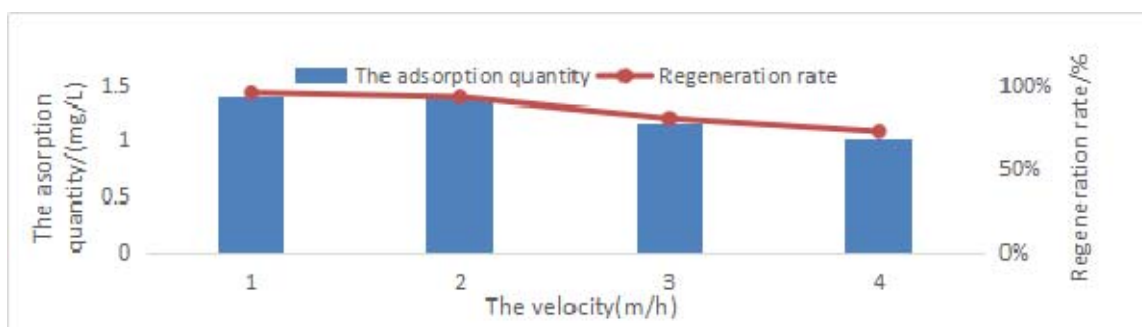


Fig.4 Velocity influence on the effect of adsorption of activated alumina recycling

Figure 4 shows that on the same test conditions, the influence of velocity on the regeneration absorption effect of activated alumina is less. Compared with the regeneration rate of 72.03% on the high-velocity condition, the regeneration on the low-velocity condition is higher, and the sufficient action of aluminum sulfate and activated alumina can be used better. When the regeneration velocity is 3m/h and the absorption quantity recovers to 1.36mg/g, the regeneration rate is 95.10%. On the basis that the regeneration absorption quantity of activated alumina recovers more, the regeneration duration time can be shortened to a shorter time.

The absorbing saturated activated alumina is generated many times, which shows that the absorption regeneration rate of the activated alumina is reduced along with the increase of regeneration times. When the regeneration times reach 18, the absorption regeneration rate of the activated alumina reduces to 1.13% and tends to be stable. At this moment, it is basically considered that even if regenerated for more times, the activated alumina loses the absorbing ability

basically and new activated alumina filter material is needed.

On the conditions that the water temperature is 15°C and pH is 7, Calcium chloride, calcium carbonate and aluminum sulfate solid of the same mole quantity are respectively thrown in three beakers of 1000ml with regenerated liquid of 500 ml. The three kinds of mixture are let stand for 1.5h. The concentration of fluoride ion in the supernatant (supernatant needs to be filtered if thrown with Calcium chloride) are measured so as to determine the best coagulant variety.

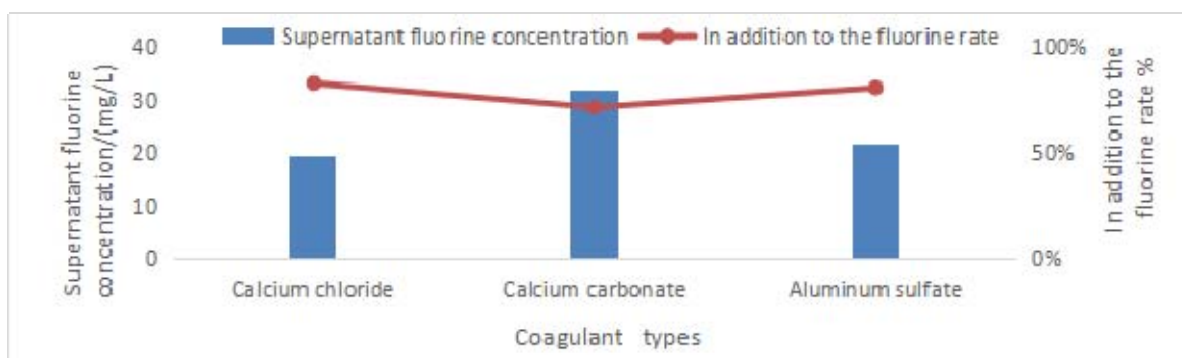


Fig.5 Three kinds of coagulants in the regenerative liquid fluorine ion removal effect of the contrast

Figure 5 shows that on the same test conditions, Calcium chloride with the same mole quantity has the best effect on removing fluoride ion. The concentration of the fluoride ion in the supernatant is 19.3mg/L, and the removal rate of fluoride ion is 82.93%. With calcium carbonate and aluminum sulfate, the concentration of the fluoride ion in the supernatant are respectively 32.0mg/L and 21.6mg/L and the removal rate of fluoride ion are respectively 71.56%、80.80%. Moreover, in the two kinds of solution, thick precipitation of different degree respectively occurs. Compared with the suspended solids in the Calcium chloride solution, the thick precipitation is difficult to remove.

The influence of the quantity of thrown Calcium chloride on the removal effect of fluoride ion in regenerated liquid

On the conditions that the water temperature is 15°C and pH is 7, Calcium chloride of 600mg, 800mg, 1000mg and 1200mg are respectively thrown in four beakers of 1L with regenerated liquid of 1000 ml. The four kinds of mixers are mixed evenly and let stand for 1.5h. The concentration of fluoride ion in the supernatant is measured so as to determine the best Calcium chloride throwing quantity.

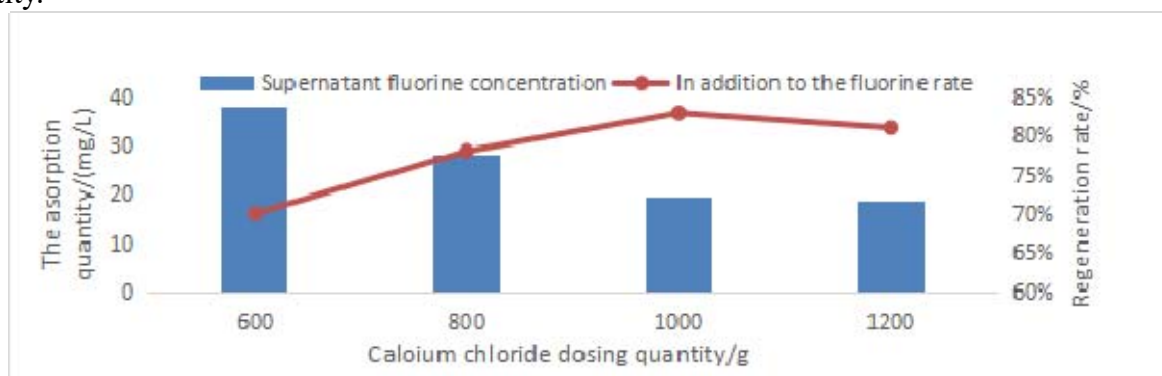


Fig.6 calcium chloride dosing quantity of removing fluorine ion in regenerative liquid

Figure 6 shows that on the same test conditions, along with the increase of the quantity of the thrown Calcium chloride, the concentration of the fluoride ion in the supernatant decreases evidently. When the quantity of thrown Calcium chloride is 1000mg/L, concentration of the fluoride ion in the supernatant is 19.2mg/L and the removal rate of fluoride ion is 82.93%. After that, along with the increase of the quantity of the thrown Calcium chloride, the concentration of the residual fluoride ion in the supernatant does not change basically. Therefore, the best quantity

of thrown Calcium chloride is 1000mg/L.

Conclusion

Through comparison, this thesis analyzes the influence of different filter materials and coagulant varieties on the fluoride ion removal effect in fluorine-containing effluent, and also studies the influence of the concentration of regenerant aluminum sulfate solution and regeneration time on the regenerating effect of activated alumina. Also, according to the test results, the best theoretical values of influence factors are determined during the courses of filtering fluoride ion removal and regeneration treatment of activated alumina. The study shows that as the filter material, the activated alumina has the best effect on removing the fluoride ion in the water sample, and the removal rate is 66.51%. On the same condition, as the coagulant, calcium chloride of the same mole quantity has the best effect on removing the fluoride ion, and the fluoride ion removal rate is 82.93%. Wherein, the best quantity of thrown Calcium chloride is 1000mg/L. On the conditions that the water temperature is 15°C, the concentration of aluminum sulfate is 3%, the regeneration time is 3h and the regeneration velocity is 3m/k, the regeneration effect is the best, and the regeneration rate reaches 95.10%.

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